UC Riverside

2017 Publications

Title

Synthesis of LiFePO₄ Using an Ionic Liquid/Water Composite Medium

Permalink

<https://escholarship.org/uc/item/5mw0z1nn>

Journal

MRS Advances, 2(17)

ISSN

2059-8521

Authors

Tith, Rany
Kwee, Darren
Jung, Kichang
et al.

Publication Date

2017-01-31

DOI

10.1557/adv.2017.132

Peer reviewed

Synthesis of LiFePO_4 Using an Ionic Liquid/Water Composite Medium

Rany Tith^{1,2}, Darren Kwee^{1,2}, Kichang Jung^{1,3}, Alfredo A. Martinez-Morales^{1,2}

¹College of Engineering, Center for Environmental Research and Technology, Riverside, CA 92507, U.S.A

²Winston Chung Global Energy Center, University of California, Riverside, CA 92521, U.S.A.

³Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521, U.S.A

ABSTRACT

In this work, we investigate a novel synthesis route for the synthesis of LiFePO_4 material that utilizes an ionic liquid/water composite medium. The effect of reaction time and reaction temperature on the crystallinity of synthesized material is investigated through X-ray diffraction (XRD). Morphology is analyzed through scanning electron microscopy (SEM). It is observed that the intensity of peaks corresponding to LiFePO_4 increase as reaction time increases, but unwanted peaks are present as well. SEM characterization indicates that various structures are initially formed, but as the reaction time progresses product morphology changes in size.

INTRODUCTION

Batteries are copiously used in a variety of applications such as mobile devices, electric vehicles and grid balancing. As a result of this, there is a critical need for energy storage devices that are sustainable and can meet modern energy and power demands. The commercialization of the lithium-ion battery began in the early 1990s with Sony [1]. These early devices used layered transition metal oxides with a graphite anode. The most widely used cathode, LiCoO_2 , is considered unsustainable due to a low abundance of cobalt in comparison to lithium [1]. Moreover, for an energy storage device to be used in daily life applications, it needs to be reliable and safe. In recent years, there has been significant research done in using phospho-olivines for rechargeable lithium-ion batteries [2]. In particular, LiFePO_4 when compared to LiCoO_2 is a competitive solution because it is intrinsically more stable, and iron being a more abundant element can replace the more rare cobalt [1]. The stability of LiFePO_4 was studied by A. Andersson et Al., reporting that at slightly elevated temperatures LiFePO_4 shows capacity improvement and no troublesome reactions such as thermal decomposition were observed at 60 °C [3].

The method used to synthesize LiFePO_4 affects the morphology and crystallinity of the product. A common procedure in industry is to utilize high temperatures (400 °C-800 °C) and dry reactant powders in a solid-state reaction process to form LiFePO_4 . This creates large particles that can be undesirable. Smaller particles are sought to create shorter diffusion pathways and larger surface area. Other methods, such as hydrothermal, requires a pressure chamber to create particles in the nanometer range. In 2009, a novel approach was developed by N. Recham et al., in which ionic liquids were used to control the morphology of synthesized LiFePO_4 material [4], which serves as one of the motivations for this work.

Since then, room temperature ionic liquids have been studied to: 1) achieve high temperature thermal stability; 2) maintain low vapor pressure; and, 3) used as solvents with the potential to be recycled [5]. This thermal stability in particular has been described by W. Feng et

al., referencing an onset of decomposition temperatures ranging from 125 °C to 424 °C [6]. Furthermore, Parnham et al. reported that water in ionic liquids could be beneficial as it can act as a mineralizer to bring insoluble precursors to seed crystals [7].

Our work attempts to understand the effects of experimental parameters on the synthesis of LiFePO_4 using an ionic liquid/water composite medium.

EXPERIMENT

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is added into DI water (type 1 defined by ISO 3696) and is stirred for 1 hour. Li_3PO_4 with 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI Otf) is added into the FeSO_4 aqueous solution. The solution is stirred and ultrasonicated for 1 hour each. The mixture is heated at 260 °C in a nitrogen environment for various times: 0 hours, 3 hours, 12 hours, 18 hours, and 36 hours. Alternatively, while keeping time constant at 36 hours, a second experiment was conducted by running two reactions with ionic liquid-only solutions: 1) at 260 °C (1:1 ionic liquid:water ratio); and, 2) at 230 °C (2:1 ionic liquid:water ratio). After each synthesis the product is cleaned with acetonitrile several times. XRD is done using a Panalytical X'Pert XRD instrument using Cu K α radiation, SEM and EDX were done with a NovaNano SEM 450.

DISCUSSION

From the diffractograms shown in Figure 1 (A-B), the gradual growth of peaks matching the database reference for LiFePO_4 are observed. This is indicative that reaction time is a key factor during the synthesis reaction. Specifically, at 29.74° 2 θ we can see a gradual growth for LiFePO_4 over time.

Figure 1. XRD pattern (A) time dependence study, (B) 20°-40° 2 θ for time dependent study.

In Figure 2 (A-B) the XRD pattern for the ionic liquid-only (260 °C), and ionic liquid/water composite (230 °C), both show a resemblance towards LiFePO_4 . Although they both indicate very similar peaks, the intensity near 29.74° 2 θ is larger for material prepared at 260 °C with just ionic liquid. A stronger peak at this point is a key characteristic of LiFePO_4 .

Furthermore, when the medium ratio is adjusted to equal parts of ionic liquid and water, peaks that are correlated with LiFePO_4 are no longer seen and only one peak is dominant (blue diffractogram).

Figure 2. XRD pattern (A) varying temperature, ionic liquid to water ratio, and ionic liquid only at 36 hours synthesis, (B) magnified axis of A between 20–40° 2θ

Shown in Figure 3(A) are the general structures formed at 12 hours into the synthesis and are highlighted in Figure 4(A) and Figure 5. More importantly, we can see the beginning of the agglomerations throughout the 18 hours synthesis (Figure 3(B)) start forming, showing similarities to the white rectangle in Figure 3(A). Furthermore, Figure 4(B) and Figure 5 specifically highlights the similarities between the two agglomerations seen at 12 hours and 18 hours.

Figure 3. SEM image of LiFePO_4 synthesized for (A) 12 hours and (B) 18 hours.

Figure 4. High magnification SEM image showing crystals synthesized at (A) 12 hours (B) 18 hours.

Figure 5. High magnification of the white box shown in SEM image 2A.

Figure 1 indicates that longer reaction time contributes to the synthesis of LiFePO_4 , yet peaks that cannot be attributed to LiFePO_4 are present. In accordance with undesired peaks, are the elements of sulfur seen throughout the synthesis at 12 hours as indicated by energy dispersion spectroscopy (Figure 6). The measured sulfur content can be possibly attributed to FeSO_4 that is used as a precursor.

Figure 6. Electron dispersion spectroscopy (EDX) of (A) Figure 3(A) and (B) Figure 4(A).

CONCLUSION

Overall, in this work we show an evaluation of parameters on a novel synthesis method using an ionic liquid/water composite medium. It is seen that reaction time plays a significant factor in obtaining a product that resembles LiFePO_4 . Moreover, varying temperature and the ionic liquid to water ratio can affect the crystallinity of the product as depicted by x-ray diffraction. In future works, we will further focus on optimizing the aforementioned parameters and investigating other variables such as pH and precursor concentration.

ACKNOWLEDGMENTS

The SEM and XRD characterization was conducted at the Central Facility for Advanced Microscopy and Microanalysis (CFAMM). This research was partially funded by the Winston Chung Global Energy Center (WCGEC).

REFERENCES

- [1] Armand, M., & Tarascon, J.-M. (2008). Building better batteries. *Nature*, 451(7179), 652–657. Retrieved from <http://www.nature.com/doifinder/10.1038/451652a>
- [2] A.K. Padhi, K.S. Nanjundaswamy, and J. B. G. (1997). Phospho-Olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries. *J. Electrochem. Soc.*, 144(4), 1–7.
- [3] A. S. Andersson, J. O. Thomas, B. Kalska, and L. Häggström, “Thermal Stability of LiFePO_4 -Based Cathodes,” *Electrochem. Solid-State Lett.*, vol. 3, no. 2, pp. 66–68, 2000.
- [4] Recham, N., Dupont, L., Courty, M., Djellab, K., Larcher, D., Armand, M., & Tarascon, J. M. (2009). Ionothermal Synthesis of Tailor-Made LiFePO_4 Powders for Li-Ion Battery Applications. *Chemistry of Materials*, 21(5), 1096–1107. <http://doi.org/10.1021/cm803259x>
- [5] Antonietti, M., Kuang, D., Smarsly, B., & Zhou, Y. (2004). Ionic Liquids for the Convenient Synthesis of Functional Nanoparticles and Other Inorganic Nanostructures. *Angewandte Chemie International Edition*, 43(38), 4988–4992. JOUR. <http://doi.org/10.1002/anie.200460091>
- [6] W. quan Feng, Y. heng Lu, Y. Chen, Y. wei Lu, and T. Yang, “Thermal stability of imidazolium-based ionic liquids investigated by TG and FTIR techniques,” *J. Therm. Anal. Calorim.*, vol. 125, no. 1, pp. 143–154, 2016.
- [7] Parnham, E. R., & Morris, R. E. (n.d.). Ionothermal Synthesis of Zeolites, Metal–Organic Frameworks, and Inorganic–Organic Hybrids. <http://doi.org/10.1021/ar700025k>